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COMMITTEE OF EXPERTS ON THE
TRANSPORT OF DANGEROUS GOODS

Sub-Committee of Experts on the
Transport of Dangerous Goods
(Fifteenth session,
Geneva, 29 June-10 July 1998,
agenda item 6 (b))

EXPLOSIVES (CLASS 1)

Proposal for a new entry for hydrazinium nitroformate in Class 1 (1.1D)

Transmitted by the Expert from the Netherlands

Introduction

1. The research on the field of propellants for space applications concentrates on increasing the performance. This is very attractive for either reducing the volume of the propellant or for increasing the pay load of a rocket system. One way of obtaining this increased performance is to apply new energetic materials in the propellant formulation.

2. One very promising candidate is Hydrazinium nitroformate (HNF). The main advantages are the high energy content (ΔH_c = - 5820 kJ/kg) and the small molecules in the decomposition products, which gives a high gas yield. The international interest in this substance is rapidly increasing, so it is expected that this substance will be transported globally in increasing amounts. At the moment the substance is produced in the Netherlands.

Properties of HNF

3. The data sheet for new classification of substances, according to Figure 1 of the Model Regulations is included in Annex. It should be stated that most of the data is for the pure substance. This chapter will give a summary of the most characteristic results.
Hydrazinium nitroformate ($N_2H_5C(NO_2)_3$) is a bright yellow crystalline salt of trinitromethane and hydrazine, with a molecular weight of about 183 kg/kmol. Its oxygen balance is +13% and the enthalpy of formation = -72 kJ/mol.
The substance is capable of detonation with a velocity of 8.4 km/s. The threshold with regards to sensitiveness to shock is comparable to that of pressed Composition B (about 3 GPa with a PPMA gap test).
The impact sensitiveness is 2 - 3 J, (determined with Test 3 (a) (ii), the BAM Fallhammer) and the friction sensitiveness is 16 - 36 N (determined with Test 3 (b) (i), the BAM friction apparatus) depending on the purity of the HNF. The thermal stability (Test 3(c)) is satisfactory, during 168 hours of testing at 75° C no temperature difference between the sample and reference material is measured. The small scale burning test (Test 3 (d)) is negative. The general conclusion is that the substance fails the friction test but passes the three other tests.
The twelve meter drop test for packaged substances (Test 4 (b) (ii)) was performed with the substance packaged in a fibre board box with good result (no fire or explosion occurred).

Phlegmatization of HNF

4. In analogy to for instance PENT, RDX and HMX (which may only be transported when phlegmatized) attempts were made to phlegmatize HNF. Addition of water, alcohol or wax did not have the desired result. Therefore, more sophisticated phlegmatizing agents need to be applied.
The phlegmatization is based on the idea of using a (semi-) liquid medium in which the HNF crystals can float and thus have the full freedom to move with the rapid movement of a shear force. This can be obtained by a non-solvent liquid with 5 - 6 % gelling agent. For further improvement a wetting agent can be used. At the moment it is not possible to process the gels with more than 40% (by weight) of HNF because of the high viscosity of such mixtures, but further research is being performed.
The results of impact and friction sensitiveness measurements with samples containing 40% HNF are 30 J and 240 N respectively. Extrapolation of the results at various loads of HNF indicates that mixtures with 60% HNF would have a friction sensitiveness of about 100 N, but this is not demonstrated by experiments yet. If the additional results are satisfactory and available in time for the Fifteenth Session, an INF.paper will be submitted presenting the results and proposing a lower phlegmatizer percentage.

5. Since the non-solvent liquid can be volatile a provision similar to Special Provision 28 of Chapter 3.3 is necessary to prevent that the concentration of phlegmatizer falls below the minimum concentration.

Proposals

6. It is proposed to include an entry in the dangerous goods list of Chapter 3.2 of the Model Regulations according to the following proposal.

UN No.	Name and Description	Class or division	Subsidiary Risks	UN packing group	Special provisions	Limited quantities	Packagings and IBCs		Portable tanks	
							Packing instruction	Special provisions	Portable tank instruction	Portable tank special provisions
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
XXXX	HYDRAZINIUM NITROFORMATE (HNF), DESENSITIZED, with not less than 60% phlegmatizer of the gel type	1.1D			266, YYY		112			

7. Insert a new special provision in Chapter 3.3 of the Model Regulations reading:

YYY The substance shall be packed so that the percentage of phlegmatizer will not fall below that stated, at any time during transport.

Alternatively, instead of inserting a new Special Provision, Special Provision 28 may be changed accordingly.

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DATA SHEET TO BE SUBMITTED TO THE UNITED NATIONS FOR NEW OR AMENDED CLASSIFICATION OF SUBSTANCES

Submitted by: **the expert from the Netherlands** Date: **April 1998** .....

Supply all relevant information including sources of basic classification data. Data should relate to the product in the form to be transported. State test methods. Answer all questions - if necessary state "not known" or "not applicable" - If data is not available in the form requested, provide what is available with details. Delete inappropriate words.

Section 1. SUBSTANCE IDENTITY

1.1 Chemical name: **Hydrazinium nitroformate** .....

1.2 Chemical formula: $N_2H_5C(NO_2)_3$ .....

1.3 Other names/synonyms: **HNF** .....

1.4.1 UN number ..... 1.4.2 CAS number .....

1.5 Proposed classification for the Recommendations

1.5.1 proper shipping name (3.1.2 */): **Hydrazinium nitroformate (HNF), Desensitized, with not less than 60% phlegmatizer of the gel type**

1.5.2 class/division: **1.1D** ..... subsidiary risk(s)

packing group: not applicable .

1.5.3 proposed special provisions: **YYY (or modified 28), 266**

1.5.4 proposed packing method: **Packing Instruction 112**

Section 2.PHYSICAL PROPERTIES

2.1 Melting point or range: **122 - 124** .... °C

2.2 Boiling point or range: **not applicable (decomposes at melting point)**

2.3 Relative density at:

2.3.1 15 °C .....

2.3.2 20 °C **1.8** .....

2.3.3 50 °C .....

2.4 Vapour pressure at:

2.4.1 50 °C ..... kPa

2.4.2 65 °C ..... kPa

2.5 Viscosity at 20 °C**/ ..... m^2/s

2.6 Solubility in water at 20 °C ~ **100** .. g/100 ml

2.7 Physical state at 20 °C (2.2.1.1*/) **solid/~~liquid/gas~~****/

2.8 Appearance at normal carriage temperatures, including colour and odour: **bright, yellow crystalline powder** .....

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*/ *This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.*

**/ *See definition of "liquid" in 1.2.1 of the Model Regulations on the Transport of Dangerous Goods.*

2.9 Other relevant physical properties .....
.....

Section 3. FLAMMABILITY

3.1 Flammable vapour

3.1.1 Flash point (2.3.3 ***/) ..... °C oc/cc

3.1.2 Is combustion sustained? (2.3.1.2*/) yes/no

3.2 Autoignition temperature ..... °C

3.3 Flammability range (LEL/UEL) ..... %

3.4 Is the substance a flammable solid? (2.4.2 */) NO

3.4.1 If yes, give details .....
.....
.....

Section 4. CHEMICAL PROPERTIES

4.1 Does the substance require inhibition/stabilization or other treatment such as nitrogen blanket to prevent hazardous reactivity ? yes/no

If yes, state

4.1.1 Inhibitor/stabilizer used .....

4.1.2 Alternative method .....

4.1.3 Time effective at 55 °C .....

4.1.4 Conditions rendering in ineffective .....

4.2 Is the substance an explosive according to paragraph 2.1.1.1? (2.1*/) yes/no

4.2.1 If yes, give details: **is manufactured to produce a practical, explosive effect, can detonate with a velocity of 8.4 km/s, the shock initiation threshold is comparable to presse Composition B, the pure substance is thermally stable, the pure substance is too sensitive to friction, the phlegmatized substance meets the requirements of Test Series 3** .....

4.3 Is the substance a desensitized explosive? (2.4.2.4*/) yes/no

4.3.1 If yes, give details .....
.....
.....

4.4 Is the substance a self-reactive substance? (2.4.1 */) yes/no

If yes, state

4.4.1 exit box of flow chart .....

What is the self accelerating decomposition temperature (SADT) for a 50 kg package? .... °C

Is the temperature control required? (2.4.2.3.4*/) yes/no

4.4.2 proposed control temperature for a 50 kg package ..... °C

4.4.3 proposed emergency temperature for a 50 kg package ..... °C

***/ *This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.*

4.5 Is the substance pyrophoric? (2.4.3 */) **yes/no**

4.5.1 If yes, give details .....

4.6 Is the substance liable to self-heating? (2.4.3 */) **yes/no**

4.6.1 If yes, give details .....

4.7 Is the substance an organic peroxide (2.5.1 */) **yes/no**

If yes state

4.7.1 exit box of flow chart .....

What is the self accelerating decomposition temperature (SADT) for a 50 kg package? °C

Is the temperature control required? (2.5.3.4.1 */) yes/no

4.7.2 proposed control temperature for a 50 kg package ..... °C

4.7.3 proposed emergency temperature for a 50 kg package ..... °C

4.8 Does the substance in contact with water emit flammable gases? (2.4.4 */) **yes/no**

4.8.1 If yes give details .....

4.9 Does the substance have oxidizing properties (2.5.1 */) **yes/no**

4.9.1 If yes, give details .....

4.10 Corrosivity (2.8 */) to:

4.10.1 mild steel ..... mm/year at ..... °C

4.10.2 aluminium ..... mm/year at ..... °C

4.10.3 other packaging materials

(specify) .... mm/year at .....

.... mm/year at .....

4.11 Other relevant chemical properties .....

Section 5, HARMFUL BIOLOGICAL EFFECTS

5.1 LD 50, oral (2.6.2.1.1 */) **128** ..... mg/kg Animal species: **rats** .....

5.2 LD 50, dermal (2.6.2.1.2 */): **not toxic** .. mg/kg Animal species: **rats** .....

5.3 LC 50, inhalation (2.6.2.1.3 */) ..... mg/litre Exposure time ..... hours
or ml/m³ ..... Animal species .....

5.4 Saturated vapour concentration at 20 °C (2.6.2.2.4.3 */) ml/m3

5.5 Skin exposure (2.8 */) results: **none irritative, non corrosive** Exposure time **4** ..... hours
Animal species: **albino rabbits**

5.6 Other data: **possibly mutagenic, based on Ames test with Salmonella typhemurium** .....

*/ *This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.*

5.7 Human experience .....
.....

Section 6. SUPPLEMENTARY INFORMATION

6.1 Recommended emergency action

6.1.1 Fire (include suitable and unsuitable extinguishing agents)
water, dry chemicals, CO_2 .....

6.1.2 Spillage **brush off and rinse with water** .....

6.2 Is it proposed to transport the substance in:

6.2.1 Intermediate Bulk Containers (6.5 */) ? **yes/no**

6.2.2 Portable tanks (6.6 */) ? **yes/no**

If yes, give details in Sections 7 and/or 8.

Section 7. INTERMEDIATE BULK CONTAINERS (IBCs) (only complete if yes in 6.2.1)

7.1 Proposed type(s) .....

Section 8. MULTIMODAL TANK TRANSPORT (only complete if yes in 6.2.2)

8.1 Description of proposed tank (including IMO tank type if known) .....
.....

8.2 Minimum test pressure .....

8.3 Minimum shell thickness .....

8.4 Details of bottom openings, if any .....

8.5 Pressure relief arrangements .....

8.6 Degree of filling .....

8.7 Unsuitable construction materials

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*/ *This and similar references are to chapters and paragraphs in the Model Regulations on the Transport of Dangerous Goods.*